IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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Applicant :   Shingo TODE et al.

Filed   :   February 1, 2006

TC/A.U.   :   1795

Examiner   :   Karie O. Apicella

Dkt. No.   :   MAM-074

Cust. No. :   20374

DECLARATION OF PRIOR INVENTION IN WTO MEMBER COUNTRY TO OVERCOME CITED PUBLICATION (37 C.F.R. § 1.131)

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

We, Shingo TODE, Akira KINOSHITA, Hiroyuki FUJIMOTO, Yasufumi TAKAHASHI, Ikuro NAKANE and Shin FUJITANI, declare and state THAT:

1.   We are the inventors of the nonaqueous electrolyte secondary battery defined in claims 1-3, 7 and 11 of the subject application.

2.   The nonaqueous electrolyte secondary battery defined in claims 1-3, 7 and 11 was reduced to practice in Japan prior to the July 30, 2003, filing date of Ohzuku et al., US 2004/0126660 A1 ("Ohzuku"); and after January 1, 1996.

3.   To establish that the nonaqueous electrolyte secondary battery defined in claims 1-3, 7 and 11 was reduced to practice in

Japan prior to July 30, 2003, the following documents, in which all dates have been redacted, are submitted herewith together with English translations as evidence:

Exhibit A: Request for New Domestic Applications dated prior to July 30, 2003,

Exhibit B: Memorandum of idea dated prior to July 30, 2003, which was attached to the above Request, and

Exhibit C: Draft specification which was also attached to the above Request.

4.   The examples in the draft specification describe tests carried out by us or under our supervision.

5.   Example 1 describes a three-electrode beaker cell (corresponding to a nonaqueous electrolyte secondary battery) in which the positive electrode material is a positive active material which includes a lithium transition metal complex oxide represented by the formula $LiMn_{0.33}Ni_{0.33}Co_{0.34}O_2$, and further includes zirconium in an amount by mole of 0.5 %, based on the total amount of the transition metals[1]. The battery was charged until the potential of the working

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[1] Example 1 of the draft specification states that "zirconium (IV) oxide was added so that a ratio in mole of zirconium to the obtained main active material $LiMn_{0.33}Ni_{0.33}Co_{0.34}O_2$ was brought to 0.5 %." A ratio in mole of zirconium to the obtained main active material is equal to a ratio in mole of zirconium to the total amount of the transition metals.

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(positive) electrode reached 4.3 V vs. Li/Li^+.

6.   Example 2 describes a battery having the same construction as the battery in Example 1 except that the amount of zirconium of the positive electrode material by mole was 1.0 %.

7.   Example 3 describes a battery having the same construction as the battery in Example 1. The charge potential of the working (positive) electrode was 4.6 V vs. Li/Li^+.

8.   Example 4 describes a battery having the same construction as the battery in Example 2. The charge potential of the working (positive) electrode was 4.6 V vs. Li/Li^+.

9.   Example 5 describes a nonaqueous electrolyte secondary battery in which the positive electrode material is a positive active material as prepared in Example 2 and which includes a lithium transition metal complex oxide represented by the formula $LiMn_{0.33}Ni_{0.33}Co_{0.34}O_2$, and further includes zirconium in an amount by mole of 1.0 %, based on the total amount of said transition metals. The negative electrode contains a graphite material. The charge voltage was 4.5 V.

10.   Fig. 4 of the draft specification is a graph showing the 2nd-cycle and 16th-cycle charge/discharge curves for the batteries of Example 3 and Comparative Example 2 at an end of charge potential of 4.6 V vs. Li/Li^+ and corresponds to the figure in the memorandum of idea.

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All statements made herein of our own knowledge are true and all statements made on information and belief are believed to be true; and that further these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent resulting therefrom.

Signed this _____ day of _____, 2010.

                    Signed:_____

                    Name: Shingo TODE

Signed this _____ day of _____, 2010.

                    Signed:_____

                    Name: Akira KINOSHITA

Signed this _____ day of _____, 2010.

                    Signed:_____

                    Name: Hiroyuki FUJIMOTO

4

Signed this _____ day of _____, 2010.

                    Signed:_____

                    Name: Yasufumi TAKAHASHI

Signed this _____ day of _____, 2010.

                    Signed:_____

                    Name: Ikuro NAKANE

Signed this _7th_ day of _September_, 2010.

                    Signed: _Shin Fujitani_

                    Name: Shin FUJITANI

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宮崎・目次特許事務所

弁理士　目次　誠　様

三洋電機株式会社　モバイルエナジーカンパニー
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専任課長　平尾宗幸

新規国内出願の依頼

前略

　いつもお世話になっております。
下記出願依頼４件につきまして、出願手続をお願い致します。
　本件に関し、内容を説明したく存じますので、打合せにご都合の良い日を連絡
ください。

　尚、お手数ではございますが、本件の受領通知をお願い致します。

草々

記

	弊社依頼番号	名称	期限	備考
1	NPX1030020	非水電解質電池		板谷
2	LCA1030057	非水電解質二次電池の使用方法		木下
3	LCA1030059	非水電解質二次電池		戸出
4	LCA1030060	非水電解質二次電池		最相

以上

(TEL : 078-993-1141、　FAX : 078-993-1095)

SANYO

企画グループ　チーフ	BUリーダー印
Signed:	（印）
Date: ＭＯＹ	

Exhibit B

部署　新型イオン電池グループ
氏名　戸出晋吾　内線　（3219）

１．【対象技術・名称など】
非水電解質二次電池

### ２．【アイデアの内容】
※〔本アイデアの概要〕

構造／方法上の特徴：電池の満充電状態における正極の充電電位が 4.5(V vs.Li/Li⁺)以上となるリチウム二次電池において、正極活物質に Li と Ni、Mn を含有し、層状構造を有するリチウム遷移金属複合酸化物を用い、この正極活物質にジルコニウムを添加したことを特徴とする。

効果：上記正極活物質を用いる場合に、ジルコニウムを添加することで、正極が 4.5(V vs.Li/Li⁺)以上となる高充電電位での充放電サイクル行っても、放電容量・平均作動電位の低下が抑制される。これより、正極の充電電位を 4.5(V vs.Li/Li⁺)以上で用いる場合においても、充放電サイクルによる劣化が少なく、エネルギー密度の高い優れる電池を提供することができる。

３．【図解説明】（別紙／裏面使用不可）
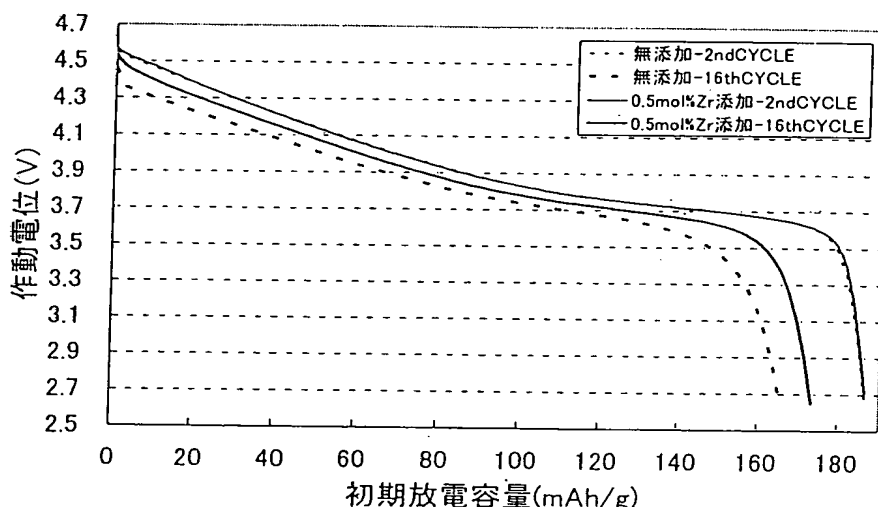
Zr を添加することによって充放電サイクル後の容量維持率が増加し平均作動電圧が上昇した

Zr 添加量	容量維持率(%)
無添加	89.2
0.5mol%	93.1
1.0mol%	92.5

Zr 添加量	平均作動電圧 (V vs Li/Li⁺)
無添加	3.834
0.5mol%	3.881
1.0mol%	3.872

図　終止電圧 4.6V(vs.Li/Li⁺)での放電曲線（2nd サイクル・16th サイクル）

４．【出願緊急度】
□実施（公表）予定があるので　　　　年　　　月　　　日迄に出願　　　　　□その他

５．【備考欄】
・層状 Mn-Ni 正極は、高充電電圧で使ってこそその特長が出せる材料です。
　その観点から重要な特許と思います。（出願）
・BASIS 対応（Mn 系材料）です。

６．【部長評価】
Ｓ・Ａ・Ｂ・Ｃ

Read and Understood by	Recorded by	部長印	チーフ印
Masakazu Itaya	*Shingo Tode*	（印）	（印）
Date:	Date:		

＊＊出願依頼時にはＳＡＰＩＯ等で先行技術調査を行うこと＊＊

（a）１～３記入後、自サイン＆証人サインの上、ラボノートに貼付
（b）４以降を、（a）のコピーに記入し完成させ、BUリーダーに提出
（c）（b）のコピーをＩＰ課への出願依頼書に添付
（d）BUリーダー押印、企画グループチーフのサイン後、ＩＰ課に転送
＊（a）～（c）は発明者、（d）はBUリーダー、企画グループが対応

Exhibit C

【書類名】明細書

【発明の名称】非水電解質二次電池

【特許請求の範囲】
　【請求項１】
　　リチウムイオンを吸蔵・放出可能な材料を用いた正極および負極と、非水電解質とを備えるリチウム二次電池において、前記正極活物質の主材が Li と Mn、Ni を含有し、層状構造を有するリチウム遷移金属複合酸化物であり、かつ該正極活物質がジルコニウムを含有していることを特徴とする非水電解質二次電池。

　【請求項２】
　　負極に炭素材料を用い、かつ 4.2V 以上で充電した際の正極と負極の充電容量比（対向する部分）が 1.0～1.3 となるようにしたことを特徴とする、請求項 1 に記載の非水電解質二次電池。

　【請求項３】
　　電池を満充電したときの正極の電位が、4.5V vs.Li/Li$^+$以上となることを特徴とする、請求項 1 または 2 に記載の非水電解質二次電池。

　【請求項４】
　　前記リチウム遷移金属複合酸化物が、化学式：Li$_a$Mn$_x$Ni$_y$Co$_z$O$_2$（0≦a≦1.2、x+y+z=1 でかつ 0＜x≦0.5、0＜y≦0.5、z≧0）で表されるものであることを特徴とする、請求項 1 または 2 に記載の非水電解質二次電池。

　【請求項５】
　　前記リチウム遷移金属複合酸化物のニッケル量とマンガン量が、実質的に等しいことを特徴とする、請求項 1～3 のいずれか一項に記載の非水電解質二次電池。

　【請求項６】
　　前記リチウム遷移金属複合酸化物の比表面積が 0.1～2.0m^2/g であることを特徴とする、請求項 1～4 のいずれか一項に記載の非水電解質二次電池。

【発明の詳細な説明】

【産業上の利用分野】
　本発明はリチウム二次電池に係わり、非水系電池の充放電サイクル特性の向上、特に高電位での充放電サイクル特性の向上を目的とした、正極の改良に関する。

【従来の技術】
　近年、金属リチウムまたはリチウムイオンを吸蔵・放出し得る合金、若しくは炭素材料などを負極活物質とし、化学式：$LiMO_2$（M は遷移金属）で表されるリチウム遷移金属複合酸化物を正極材料とする非水電解質電池が、高エネルギー密度を有する電池として注目されている。
　上記リチウム遷移金属複合酸化物の例としては、リチウムコバルト複合酸化物（$LiCoO_2$）が代表的なものとして挙げられ、既に非水電解質二次電池の正極活物質として実用化されている。しかし、遷移金属として Mn を含むものや Ni を含むものも検討されており、また、これらの三種類の遷移金属元素全てを含む材料系も盛んに検討がなされてきた（例えば、特許 2561556 号、特許 3244314 号、Journal of Power Sources 90 (2000) 176-181）。こうした Mn、Ni、Co を含むリチウム遷移金属酸化物の中で、Mn と Ni の組成が等しい化学式：$LiMn_xNi_xCo_{(1-2x)}O_2$ で現される材料が、充電状態（高い酸化状態）でも特異的に高い熱的安定性を示すことが、Electrochemical and Solid-State Letters, 4(12) A200-A203 (2001)などで報告されている。また、特開平 2002-42813 には Ni と Mn が実質的に等しい複合酸化物が、$LiCoO_2$ と同等の 4V 近傍の電圧を有し、かつ高容量で優れた充放電効率を示すことが報告されている。このような、Mn と Ni と Co を含み、層状構造を有するリチウム遷移金属複合酸化物（例えば、化学式：$Li_aMn_bNi_bCo_{(1-2b)}O_2$（$0 \leqq a \leqq 1.1$，$0 < b \leqq 0.5$））を主材（50 重量％以上）とする正極を用いた電池は、充電時の高い熱的安定性を有することから電池の信頼性が飛躍的に向上することが期待できる。さらに、このような Mn と Ni と Co を含み、層状構造を有するリチウム遷移金属複合酸化物は、その高い構造安定性から、現状の充電電圧より高く設定しても（正極の電位で 4.5V vs.Li/Li^+以上）、現在使用されている $LiCoO_2$ などより良好なサイクル特性を示すことが報告されている（Chemistry Letters, 2001, P.642-643）。現在、リチウム含有遷移金属酸化物（例えば、$LiCoO_2$）を正極に用い、負極に炭素材料を用いる非水電解質二次電池では、その充電終止電圧は一般に 4.1～4.2V となっているが、この場合では正極は理論容量に対して 50～60％しか利用されていない。したがって、Mn と Ni と Co を含み、層状構造を有するリチウム遷移金属複合酸化物を用いれば、充電電圧を高く設定しても熱的安定性を大きく低下させることなく、正極の容量を理論容量に対して 70％以上で利用することも可能であり、電池の高容量化・高エネルギー密度化が可能となる。

【発明が解決しようとする課題】
　しかし、Mn と Ni と Co を含み、層状構造を有するリチウム遷移金属複合酸化物を正極活

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物質として用いた場合でも、依然として充放電サイクルに伴う作動電圧・放電容量の低下は見られ、特に正極の充電電位が 4.5V vs.Li/Li+ 以上となるような高電位充電状態では、充放電サイクル後の作動電圧・放電容量の低下が大きく、エネルギー密度の低下が問題となっていた。すなわち、電池の充放電サイクル特性、特に満充電状態での正極の電位が 4.5V vs.Li/Li+ 以上となる電池（例えば、負極の充電電位が 0.1V vs.Li/Li+ である炭素負極を用いる場合であれば、充電電圧が 4.4V 以上となる電池）の充放電サイクル特性に課題があった。

　本発明の目的は、Mn と Ni を含み、層状構造を有するリチウム遷移金属複合酸化物を主材とする正極を用いたリチウム二次電池において、充放電サイクル特性、特に満充電状態での前記正極の電位が 4.5V（vs.Li/Li+）以上になる場合においても、充放電サイクルによる作動電圧・放電容量の低下が小さく、サイクル特性の優れた二次電池を提供することにある。

【課題を解決するための手段】

　上記の目的を達成するために、本発明が提供する非水電解質二次電池は、リチウムイオンを吸蔵・放出可能な材料を用いた正極および負極と、非水電解質とを備えるリチウム二次電池において、正極活物質の主材が Li と Mn、Ni を含有し、層状構造を有するリチウム遷移金属複合酸化物であり、かつ該正極活物質がジルコニウムを含有していることを特徴とする。

　ここで、正極に $LiCoO_2$ を用い、負極に炭素材料や Li 合金材料を用いる従来の電池では、電池の充電電圧としては 4.1～4.2V であり、負極に炭素材料を用いた場合では充電状態での正極の電位は 4.2～4.3V（vs.Li/Li+）となる。また前記電圧で充電した際の対向容量比は一般的に 1.0～1.3 となるように設計されている（正極の充電量＜負極の充電量）。このように設計されている理由は、この充電容量比が 1 を下回る場合は前記炭素材料・合金材料表面に金属リチウムが析出し、電池のサイクル特性や安全性が著しく低下し、充電容量比が 1.3 を超えると反応に関与しない余分な負極が増えるため電池のエネルギー密度が低下する。

　従って、本件に係かる非水電解質二次電池では、負極に炭素材料や Li 合金材料などのリチウムを吸蔵・放出が可能な材料を用い、電池の充電電圧を 4.2V 以上、充電状態での正極の電位は 4.3～5.2V vs.Li/Li+ とし、その電圧で充電した際の対向容量比が 1.0～1.3 となるようなものが代表的なものとして例示される。尚、正極の電位が 5.2V vs.Li/Li+ を超える領域まで充電すると、活物質中のリチウムの脱離反応よりも電極表面での電解液の分解反応のほうが顕著となるため、正極の充電電位としては前述のような範囲となる。

　また、前記ジルコニウムを含有するリチウム遷移金属複合酸化物としては、化学式：$Li_aMn_xNi_yCo_zO_2$（$0 \leq a \leq 1.2$、$x+y+z=1$ でかつ $0<x \leq 0.5$、$0<y \leq 0.5$、$z \geq 0$）で表されるものであることが好ましく、さらにはマンガン量とニッケル量が実質的に等しいことが好ましい。また、高電位下での正極活物質と電解質との反応を抑えるために、正極活物質の比表面積としては 0.1～2.0㎡/g の範囲が望ましい。

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本件で用いる非水電解質の溶媒としては高い誘電率を有する環状カーボネートと、粘性の低い鎖状カーボネートの混合溶媒を用いることが望ましいが、環状カーボネートは高電位下での酸化分解を生じやすいことから、その混合比としては 10〜30vol%が望ましい。また、正極の集電体としては厚み 10〜30μm のアルミニウム箔が一般的に用いられるが、このような集電体を用いた場合、高電位下（4.5V vs.Li/Li⁺以上）では箔そのものの腐食が進行する可能性があるため、そのような腐食を抑制する作用がある（フッ化アルミニウムの不動態皮膜が形成されるためと考えられる）LiPF$_6$ を支持塩として含むことが望ましい。更に、正極が高電位になった場合は、導電剤として用いる炭素表面上での電解液の酸化分解も進行しやすくなるため、正極中に含まれる導電剤としての炭素の量は 5wt%以下が望ましい。

【作用】

　前記 Li と Mn、Ni を含み、層状構造を有するリチウム遷移金属複合酸化物を正極活物質とする電極において、前記正極活物質にジルコニウムが含まれることにより、充放電サイクルにおける作動電圧、および容量の低下を抑制する機構については、詳細は明確ではないものの、充放電サイクル後の正負極を解析した結果、

1) Zr を含まない、上記層状構造を有するリチウム遷移金属複合酸化物について、サイクル前後の XRD パターンを調べた結果、両者で殆ど差は認められなかった。

2) サイクル後の負極に析出（または堆積）した Mn 量を調べた結果、Zr を含まない、上記層状構造を有するリチウム遷移金属複合酸化物を正極活物質とした電池では、Zr を含む場合と比較して、多量の Mn が負極に析出している。

ことがわかった（参考実験参照）。このことから、前記 Li と Mn、Ni を含み、層状構造を有するリチウム遷移金属複合酸化物を正極活物質とした電池の充放電サイクルによる特性低下は、正極活物質の構造崩壊ではなく、正極活物質表面から Mn が溶解し（溶解した Mn が負極に析出）、その結果として正極－電解液界面の抵抗が上昇して作動電圧・放電容量が低下するものと考えられる。また、充放電サイクルに対するジルコニウムの添加効果は、4.3V vs.Li/Li⁺の充電状態でも確認されるが、4.5V vs.Li/Li⁺以上の高電位な充電状態の場合、特に作動電位の低下抑制効果も大きくなる（表２および図２〜５、または表３〜５参照）。

　層状構造を有し、LiMO$_2$（M:遷移金属）で表されるリチウム遷移金属複合酸化物に Zr を添加する例としては特許第 2855877 号が挙げられるが、概特許公報では LiCoO$_2$ 粒子の表面が酸化ジルコニウム(Ⅳ)、もしくはリチウムとジルコニウムとの複合酸化物 Li$_2$ZrO$_3$ に覆われることによって安定されるため電解液の分解や結晶破壊を起こさなくなることが【0008】に記載されており、本件とは全く異なる作用・効果であると考えられる。

　前記リチウム含有複合酸化物のマンガン量とニッケル量は、容量は小さいが充電時の熱

安定性が高いマンガンの性質と、容量は大きいが充電時の熱安定性が低いニッケルの性質とを最もバランスさせるため、実質的に等しいことが望ましい。

　ジルコニウムの量が少なすぎると、高電位充放電サイクルに対する効果が現れず、一方、ジルコニウムの量が多すぎると、正極の放電特性に悪影響を及ぼす可能性があるため、正極活物質中に含まれるジルコニウムの量は、リチウム遷移金属複合酸化物に対して、0.1mol%以上5mol%以下であることが望ましい。

【発明の実施の形態】

　以下、本発明を実施例に基づき更に詳細に説明するが、本発明は下記実施例により何ら限定されるものではなく、その要旨を変更しない範囲において適宜変更して実施することが可能なものである。

【実施例】

　以下に記載した方法により、三電極式ビーカーセルを作製し、それを充放電することにより電極の充放電サイクル特性を評価した。

＜実験1＞

（実施例1）

[正極活物質の作製]

　LiOH と、$Mn_{0.33}Ni_{0.33}Co_{0.34}(OH)_2$ で表される共沈水酸化物を、Li と遷移金属全体のモル比が 1:1 になるように、石川式らいかい乳鉢にて混合した後、酸化ジルコニウム(IV)を、得られる主活物質 $LiMn_{0.33}Ni_{0.33}Co_{0.34}O_2$ に対し 0.5mol%になるように添加し、空気雰囲気中にて 1000℃で 20 時間熱処理後に粉砕し、平均粒子径が約 10μm の $LiMn_{0.33}Ni_{0.33}Co_{0.34}O_2$ で表されるリチウム遷移金属複合酸化物を得た。尚、得られた $LiMn_{0.33}Ni_{0.33}Co_{0.34}O_2$ の BET 比表面積は 0.67m²/g であった

[作用極の作製]

　このようにして得た正極活物質に、導電剤として炭素と、結着剤としてポリフッ化ビニリデンと、分散媒としての N-メチル-2-ピロリドンを、活物質と導電剤と結着剤の重量比が 90:5:5 の比率になるようにして加えた後に混練して、正極スラリーを作製した。作製したスラリーを集電体としてのアルミニウム箔上に塗布した後、乾燥し、その後圧延ローラーを用いて圧延し、集電タブを取り付けることで、作用極を作製した。

[電解液の作製]

　エチレンカーボネート（EC）とエチルメチルカーボネート（EMC）とを体積比 3：7 で混合した溶媒に対し、ヘキサフルオロリン酸リチウム（$LiPF_6$）を濃度が 1mol/l となるように溶解して、電解液を作製した。

[三電極式ビーカーセルの作製]
　Ar雰囲気下のグローブボックス中にて、図1に示す通りの三電極式ビーカーセルを作製した。尚、対極および参照極としてはリチウム金属を用いた。

[初期充放電特性の評価]
　作製した三電極式ビーカーセルを、室温にて、0.75mA/cm² （約 0.3C）の定電流で、作用極の電位が 4.3 vs. Li/Li⁺に達するまで充電し、さらに、0.25mA/cm²（約 0.1C）の定電流で、電位が 4.3V vs. Li/Li⁺に達するまで充電した後、0.75mA/cm²（約 0.3C）の定電流で、電位が 2.75V vs. Li/Li⁺に達するまで放電することにより、初期の充放電特性を評価した。

[充放電サイクル特性の評価]
　初期充放電特性を評価した後、室温にて、初期充放電特性の評価と同じ条件にて充放電を 15 サイクル行い、16 サイクルでの容量維持率を以下の式で求めた。また、1 サイクル目の放電曲線と 16 サイクル目の放電曲線を比較し、平均電極電位の低下と放電開始時の電位の低下を求めた。

　容量維持率(%)　＝　（16 サイクル目の放電容量）÷（1 サイクル目の放電容量）×100

（実施例2）
　正極活物質の作製において、熱処理後の $LiMn_{0.33}Ni_{0.33}Co_{0.34}O_2$ 中に含まれるジルコニウムの量が 1.0mol%となるようにして添加したこと以外は、実施例1と同様にして三電極式ビーカーセルを作製した。尚、得られた $LiMn_{0.33}Ni_{0.33}Co_{0.34}O_2$ の BET 比表面積は 0.64m²/g であった。初期充放電特性、充放電サイクル特性は、実施例1と同様にして評価した。

（実施例3）
　実施例1と同様にして三電極式ビーカーセルを作製した。
　初期充放電特性、充放電サイクル特性の評価において、作用極の充電電位を 4.6V vs. Li/Li⁺とした以外は、実施例1と同様にして評価した。

（実施例4）
　実施例2と同様にして三電極式ビーカーセルを作製した。
　初期充放電特性、充放電サイクル特性の評価において、作用極の充電電位を 4.6V vs. Li/Li⁺とした以外は、実施例1と同様にして評価した。

（比較例1）
正極活物質の作製において、LiOH と $Mn_{0.33}Ni_{0.33}Co_{0.34}(OH)_2$ で表される共沈水酸化物を、Li と遷移金属全体のモル比が 1:1 になるようにして、石川式らいかい乳鉢にて混合したこと以外は、実施例1と同様にして三電極式ビーカーセルを作製し、実施例1と同様にして初期充放電特性、充放電サイクル特性を評価した。

（比較例２）
　比較例１と同様にして三電極式ビーカーセルを作製した。
　初期充放電特性、充放電サイクル特性の評価において、作用極の充電電位を 4.6V vs. Li/Li$^+$とした以外は、実施例１と同様にして評価した。

　上記のようにして作製した実施例１～４の三電極式ビーカーセル A1～A4 及び比較例１、２の三電極式ビーカーセル X1、X2 の初期充放電特性および充放電サイクル特性を評価した結果を表１～２、及び図２～５に示した。また、表１には本件実施例・比較例で作製した正極材料の比表面積もあわせて記載した。

（表１）本件実施例１～４、比較例１～２に係る電池の初期充放電特性

	セル	活物質中のZr含有量（mol%）	充電終止電位（V vs.Li/Li$^+$）	比表面積（m²/g）	初期充放電効率（%）	放電容量（mAh/g）	平均電極電位（V vs.Li/Li$^+$）
比較例１	X1	0		0.67	84.5	149.0	3.784
実施例１	A1	0.5	4.3	0.67	85.0	149.4	3.809
実施例２	A2	1.0		0.63	85.6	150.8	3.806
比較例２	X2	0		0.67	84.5	186.8	3.928
実施例３	A3	0.5	4.6	0.67	85.1	186.7	3.927
実施例４	A4	1.0		0.63	84.9	187.4	3.923

（表２）本件実施例１～４、比較例１～２に係る電池の充放電サイクル特性の評価結果

	セル	活物質中のZr含有量（mol%）	充電終止電位（V vs.Li/Li$^+$）	サイクル前後での放電開始電位低下値（mV）	サイクル前後での平均電極電位低下値（mV）	容量維持率（%）
比較例１	X1	0		56	14	94.5
実施例１	A1	0.5	4.3	15	16	97.7
実施例２	A2	1.0		14	21	97.1
比較例２	X2	0		156	94	89.2
実施例３	A3	0.5	4.6	55	46	93.1
実施例４	A4	1.0		64	51	92.5

　表２から明らかなように、ジルコニウムの添加により LiMn$_{0.33}$Ni$_{0.33}$Co$_{0.34}$O$_2$ の充放電サイクル前後の容量維持率は向上し、放電開始電位の低下が抑制されている。　また、実施例１～２と実施例３～４を比較すると、充電終止電位が 4.5V vs.Li/Li$^+$以上の実施例３～４では放電開始電位の低下がジルコニウムを添加していない比較例２よりも約 100mV 改善されており、特に効果が大きいことがわかった。

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また、表2および図2～5から明らかなように、$LiMn_{0.33}Ni_{0.33}Co_{0.34}O_2$ の充放電サイクル前後の平均電極電位の低下の度合いは、4.3V vs.Li/Li⁺の充電終止では、ジルコニウムの添加効果は認められないのに対して、4.6V vs.Li/Li⁺充電終止では、ジルコニウムの含有量が増すのに伴い平均電極電位の低下が抑制されることがわかる。

このように、Li と Mn、Ni を含み、層状構造を有するリチウム遷移金属複合酸化物へのジルコニウムの添加は、従来の充電電圧（正極の電位で 4.2～4.3V vs.Li/Li⁺）よりも高くした場合に（正極の電位で 4.5V vs.Li/Li⁺以上）、特に効果が大きくなることがわかった。

＜実験2＞

以下に記載した方法により電池を作製し、初期の充放電特性および充放電サイクル特性を評価した。

（実施例5）
［正極の作製］
実施例2で作製した正極活物質と、導電剤として炭素と、結着剤としてポリフッ化ビニリデンと、分散媒としての N-メチル-2-ピロリドンを、活物質と導電剤と結着剤の重量比が 90:5:5 の比率になるようにして加えた後に混練して、正極スラリーを作製した。作製したスラリーを集電体としてのアルミニウム箔上に塗布した後、乾燥し、その後圧延ローラーを用いて圧延し、集電タブを取り付けることで、正極を作製した。

［負極の作製］
増粘剤であるカルボキシメチルセルロースを水に溶かした水溶液中に、負極活物質として人造黒鉛と、結着剤としてのスチレン－ブタジエンゴムとを、活物質と結着剤と増粘剤の重量比が 95:3:2 の比率になるようにして加えた後に混練して、負極スラリーを作製した。作製したスラリーを集電体としての銅箔上に塗布した後、乾燥し、その後圧延ローラーを用いて圧延し、集電タブを取り付けることで、負極を作製した。

［電解液の作製］
エチレンカーボネート（EC）とエチルメチルカーボネート（EMC）とを体積比 3：7 で混合した溶媒に対し、$LiPF_6$ を 1mol/l 溶解して、電解液を作製した。

［電池の作製］
正極および負極を、セパレーターを介して対向するように巻取って巻取り体を作製し、Ar 雰囲気下のグローブボックス中にて、巻取り体を電解液とともにアルミニウムラミネートに封入することにより、電池規格サイズとして、厚み 3.6mm×幅 3.5cm×長さ 6.2cm の非水電解質二次電池 A5 を得た。なお、正負極の対向容量比は 1.15 とした。

（比較例3）
比較例1で用いた正極活物質に用いた以外は、実施例5と同様にして電池を作製および評価を行った。

[電池の初期充放電特性の評価]

　作製した非水電解質二次電池を、室温にて、650mA(約 1.1C)の定電流で、電圧が 4.5V に達するまで充電し、さらに、4.5V の定電圧で電流値が 32mA(約 0.06C)になるまで充電した後、650mA の定電流で、電圧が 2.75V に達するまで放電することにより、電池の放電容量(mAh)を測定した。

[充放電サイクル特性の評価]

　　上記の電池の初期充放電特性評価後、同条件で充放電サイクル試験を行い、50 サイクル目での容量維持率と放電開始電圧の変化を求め、結果を表 3 に示した。尚、容量維持率は以下の式により算出した。

　　容量維持率(%) = (50 サイクル目の放電容量)÷(1 サイクル目の放電容量)×100

（表 3） 電池特性評価結果

	セル	充電電圧(V)	活物質中のZr 含有量(mol%)	初期放電容量(mAh)	初期充放電効率(%)	50 サイクル後容量維持率(%)	サイクル前後での放電開始電圧低下値(mV)
実施例 5	A5	4.5	1.0	642.7	82.1	92.2	67
比較例 3	X3	4.5	0	629.7	83.0	91.3	95

表 3 から明らかなように、Zr を添加した本件実施例 5 に係る電池は、Zr を添加していない比較例 3 の電池よりも、50 サイクル後の容量維持率、及びサイクル後での放電開始電圧の低下が改善されていることがわかる。

＜参考実験＞

本項では、Li と Mn、Ni を含み、層状構造を有するリチウム遷移金属複合酸化物の充放電サイクルによる作動電圧低下と放電容量低下の要因、及びジルコニウムを含有させることによる作用・効果を調べるため、以下の実験を行った。

① 充放電サイクル前後での正極活物質の XRD 測定

比較例 3 の電池について、充放電サイクルを行う前、及びサイクル後の正極を回収し、CuKαを線源とする X 線回折を行なった。その結果を図 6 に示す。さらに格子定数と、Gauss 法を用いて半価幅を算出した。結果を表 6 に示す。

（表４）充放電サイクル試験後の正極の格子定数および半価幅

	電池	充放電サイクル	半価幅（deg）		
			003面	104面	110面
比較例3	X3	サイクル前	0.1423	0.2244	0.2555
	X3	サイクル後	0.1539	0.2444	0.3006

　　図６から明らかなように、充放電サイクル前後の電池の正極のX線回折パターンに、大きな違いは見られなかった。また、表４から明らかなように、サイクル前後の電池の正極の半価幅にも大きな差は確認されなかった。これらのことから、サイクル後の電池の正極活物質についても、結晶構造バルクの崩壊などは起こっていないことが分かった。

② 　サイクル後電池の負極上へのMn析出量の評価

　　実施例５および比較例３に係る電池を充放電サイクル後、解体して負極を回収し、ロジウムを線源とする蛍光X線分析を用いて、負極表面上へのMnの溶出を測定し、（検出範囲は0-40keV）その結果を表４に示した。

（表５）電池特性評価結果

	活物質中のZr含有量（mol%）	負極上へのMn析出量（cps/μA）
実施例5	0.1	1.901
比較例3	0	2.262

　　表４から明らかなように、ジルコニウムを添加した本件実施例５に係る電池では、充放電サイクル後の負極上に析出しているMnの量が、ジルコニウムを含まない本件比較例３に係る電池よりも10%以上少なくなっていることがわかる。

　　以上、これら参考実験の結果から、LiとMn、Niを含み、層状構造を有するリチウム遷移金属複合酸化物の充放電サイクルによる作動電圧低下と放電容量低下の要因は、充放電サイクルによる正極活物質の結晶バルクの構造崩壊ではなく、充放電サイクルによる正極活物質からのMn溶出（及びそれに起因する正極－電解液界面の抵抗増加）が要因と考えられる。また、本件実施例に係る正極活物質のように、ジルコニウムを含有させることで前述のMn溶出が抑制され、充放電サイクルによる作動電圧低下・容量低下が抑えられるものと推察される。

【発明の効果】
　　以上詳述したように、リチウムイオンを吸蔵・放出可能な材料を用いた正極および負極と、非水電解質とを備えたリチウム二次電池において、正極活物質の主材がLiとMn、Niを含有し、層状構造を有するリチウム遷移金属複合酸化物であり、該正極活物質がジルコニウムを含有していることにより、充放電サイクルによる劣化が抑制され、サイクル特性に優れる非水電解質二次電池を提供することができる。

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【図面の簡単な説明】

　【図1】三電極式ビーカーセルの概略図
　　1：作用極，　2：対極（リチウム金属），　3：参照極（リチウム），　4：電解液

　【図2】本件実施例1、及び比較例1に係る電池（A1、X1）の2サイクル目、および16
　　　　サイクル目の充放電曲線：4.3V vs.Li/Li$^+$充電終止

　【図3】本件実施例2、及び比較例1に係る電池（A2、X1）の2サイクル目、および16
　　　　サイクル目の充放電曲線：4.3V vs.Li/Li$^+$充電終止

　【図4】本件実施例3、及び比較例2に係る電池（A3、X2）の2サイクル目、および16
　　　　サイクル目の充放電曲線：4.6V vs.Li/Li$^+$充電終止

　【図5】本件実施例4、及び比較例2に係る電池（A4、X2）の2サイクル目、および16
　　　　サイクル目の充放電曲線：4.6V vs.Li/Li$^+$ 充電終止

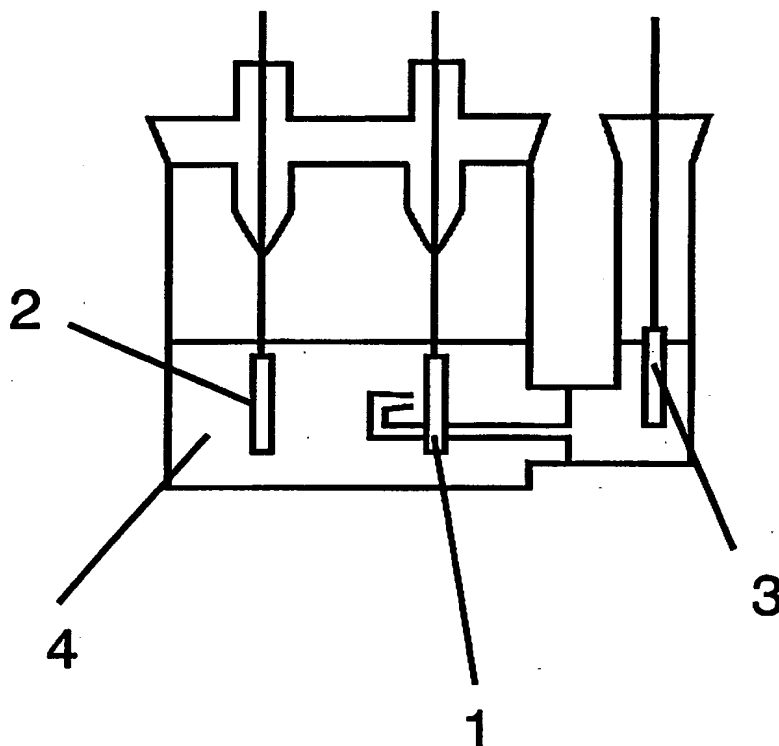　【図6】本件比較例3に係る電池（X3）の充放電サイクル試験前後における正極の X 線
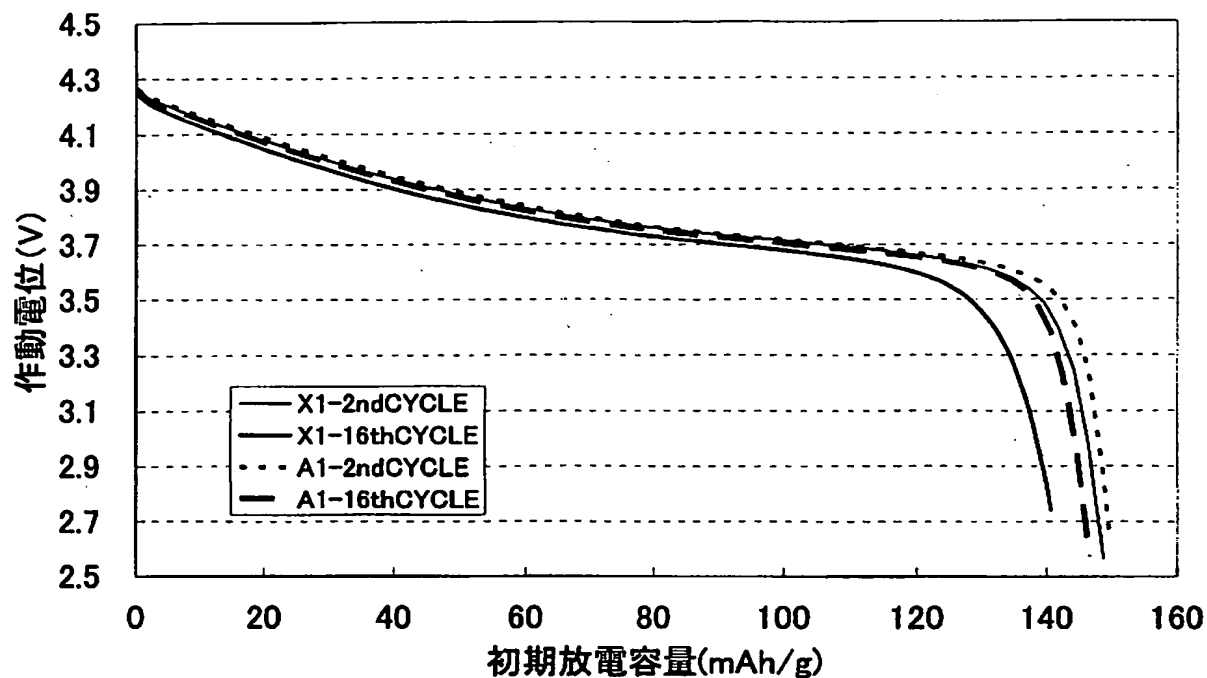　　　　回折パターン

図1　三電極式ビーカーセルの概略図

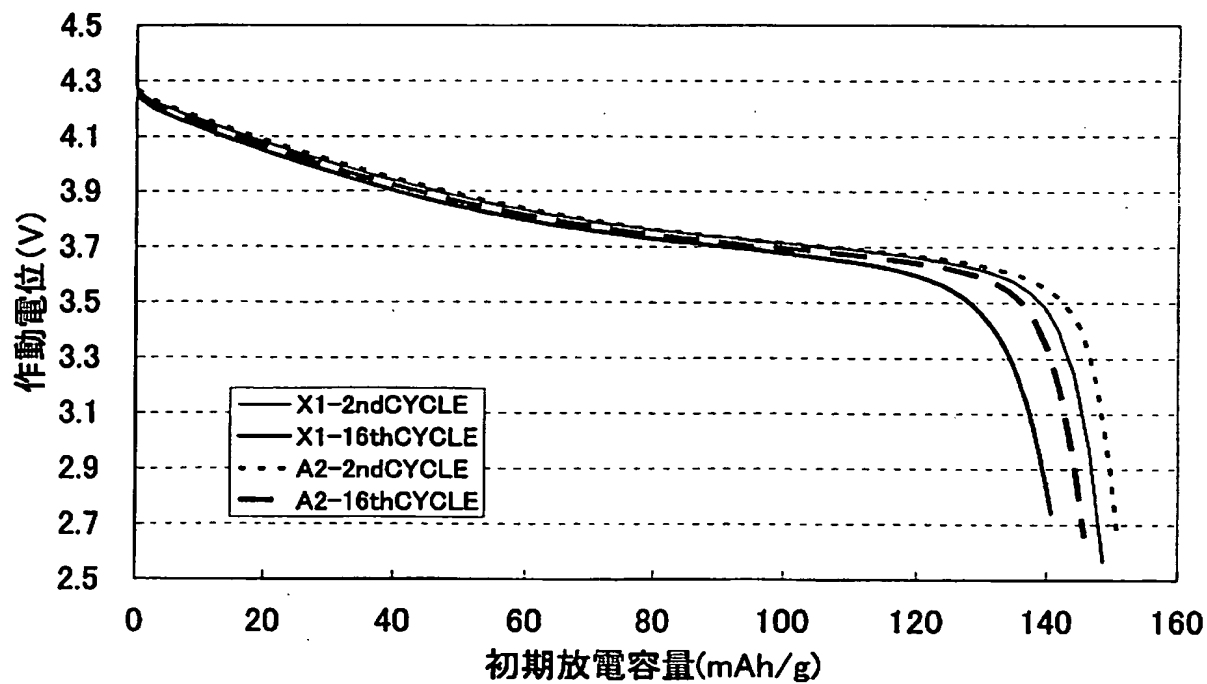図2　本件実施例1、及び比較例1に係る電池（A1、X1）の 2 サイクル目、
および16 サイクル目の充放電曲線：4.3V vs.Li/Li⁺充電終止

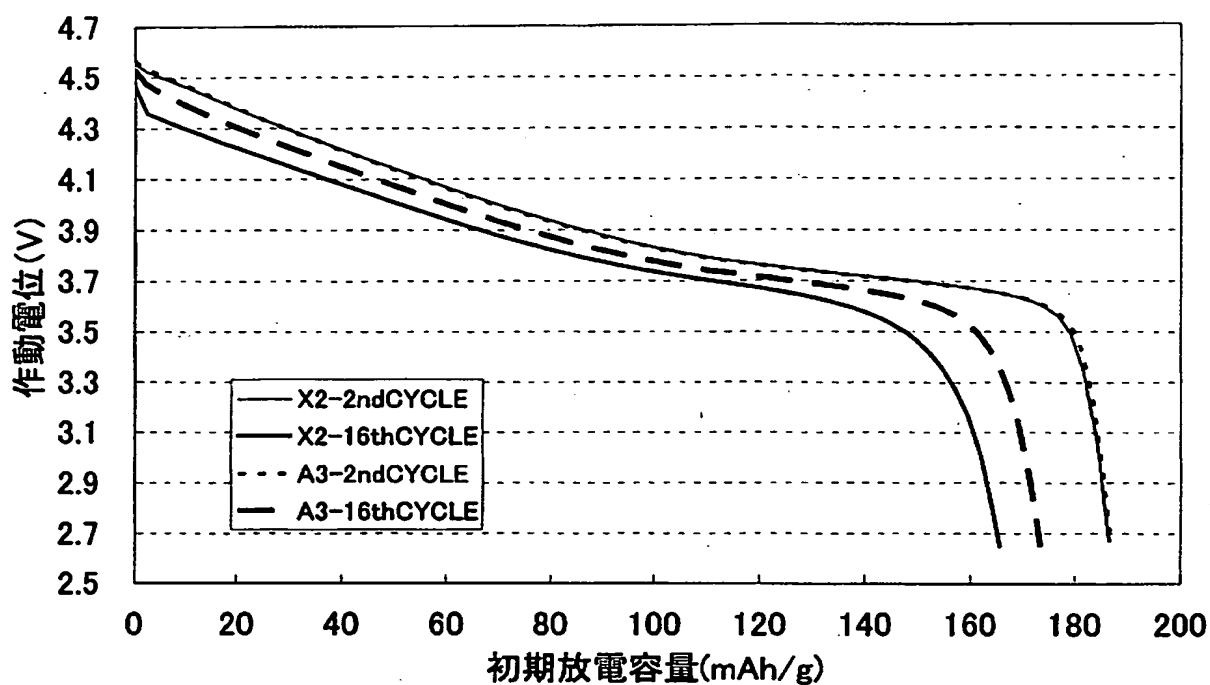図3　本件実施例2、及び比較例1に係る電池（A2、X1）の 2 サイクル目、およ
び16 サイクル目の充放電曲線：4.3V vs.Li/Li⁺充電終止

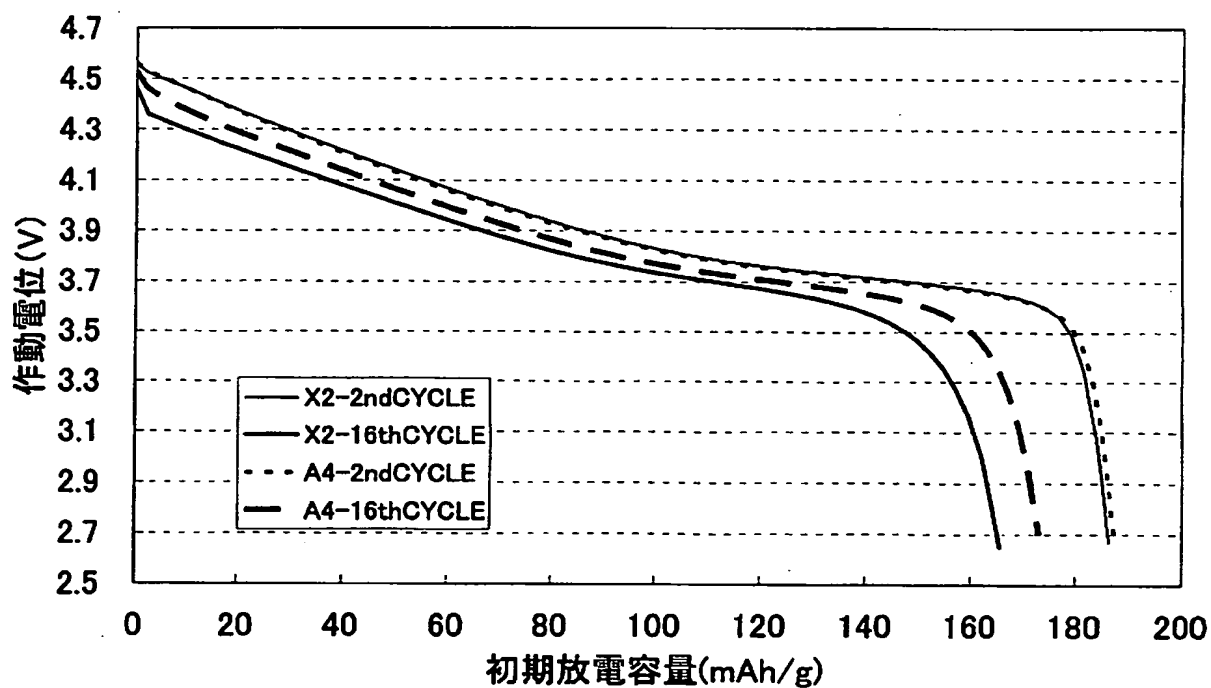図4　本件実施例3、及び比較例2に係る電池（A3、X2）の2サイクル目、および16サイクル目の充放電曲線：4.6V vs.Li/Li⁺充電終止

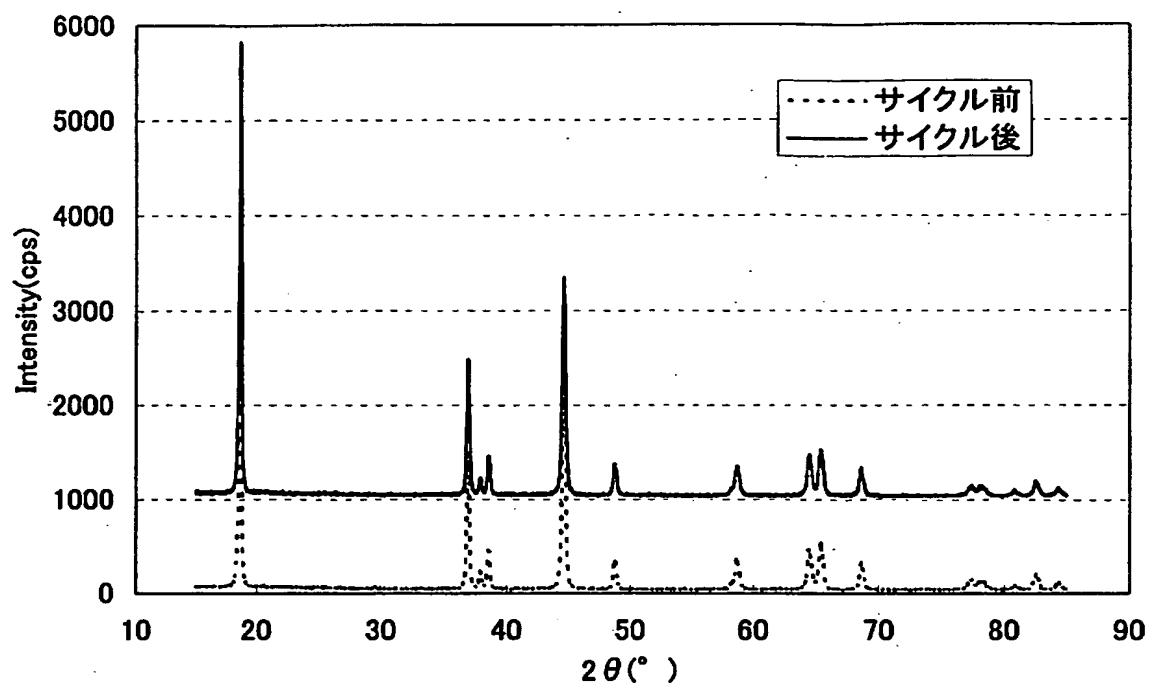図5　本件実施例4、及び比較例2に係る電池（A4、X2）の2サイクル目、および16サイクル目の充放電曲線：4.6V vs.Li/Li⁺充電終止

図6　本件比較例3に係る電池（X3）の充放電サイクル試験前後における
正極のＸ線回折パターン

Exhibit A

Dear Patent Attorney Makoto METSUGI

MIYAZAKI & METSUGI PATENT ATTORNEYS
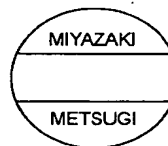
SANYO ELECTRIC CO., LTD. Mobile Energy Company

IP/ Legal Business Unit

Legal and Intellectual property Department, IP division (Seishin)

Chief Muneyuki HIRAO

Re: Request for New Domestic Applications

Thank you for your continued business.

We would like to request for the following four application procedures.

Regarding these applications, we will explain the content. Please let us know the date that would suit your convenience for the meeting.

We should appreciate your acknowledging receipt of this letter.

Notes

	Our Reference No.	Title	Due Date	Remarks
1	NPX1030020	Nonaqueous Electrolyte Battery		Itaya
2	LCA1030057	Method for Using Nonaqueous Electrolyte Secondary Battery		Kinoshita
3	LCA1030059	Nonaqueous Electrolyte Secondary Battery		Tode
4	LCA1030060	Nonaqueous Electrolyte Secondary Battery		Saishou

(TEL:078-993-1141, FAX:078-993-1095)

SANYO

Chief of the Planning Group	BU leader's Seal
Signed : Date:	

Exhibit B

Department   New Type Ion Battery Group
Name   Shingo TODE   ext. (3219)

1. [Subject matter · Title etc.]
NONAQUEOUS ELECTROLYTE SECONDARY BATTERY

2. [Content of ideas]
※[Outline of ideas]
Structural/methodological Feature: A lithium secondary battery in which the positive electrode in a fully charged state has a potential of at least 4.5 V (vs. Li /Li$^+$), characterized in that a lithium transition metal complex oxide containing Li, Ni and Mn and having a layered structure is used as a positive active material, and the positive active material further contains zirconium.

Effect: When using the positive electrode, inclusion of zirconium suppresses declining of discharge capacity and average working potential even if charge-discharge cycle is performed when the positive electrode has a high charging potential of at least 4.5 (V vs. Li/Li$^+$). Therefore, it is possible to provide an excellent battery which shows less deterioration by charge-discharge cycle and has a high energy density even if the positive electrode has a charging potential of at least 4.5 (V vs. Li/Li$^+$).

3. [Graphic explanation] (A separate sheet/reverse side is unusable)

Legend:
- · · · additive-free-2ndCYCLE
- − − additive-free-16thCYCLE
- —— 0.5mol%Zr added-2ndCYCLE
- —— 0.5mol%Zr added-16thCYCLE

Y-axis: Operating Voltage (V)
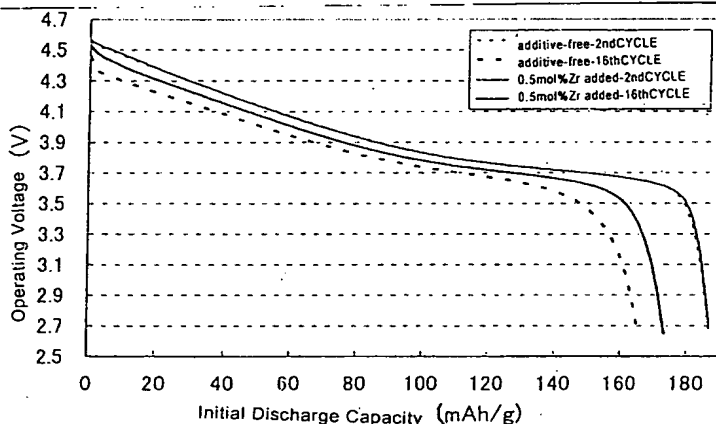X-axis: Initial Discharge Capacity (mAh/g)

Fig. Discharge Curves at an end voltage of 4.6 V (vs. Li/Li$^+$) (2nd CYCLE · 16th CYCLE)

Inclusion of Zr increased a capacity retention and an average working voltage after charge-discharge cycle.

Zr additive amount	Capacity retention (%)
additive-free	89.2
0.5mol%	93.1
1.0mol%	92.5

Zr additive amount	Average Working Voltage(V vs Li/Li$^+$)
additive-free	3.834
0.5mol%	3.881
1.0mol%	3.872

4. [Urgency of application]
☐ filling by   ,   due to the schedule for implementation (publication)   ☐Other

5. [Remarks]
· A layered Mn-Ni positive electrode is a material which shows its characteristics when used at a high charging voltage.   From this standpoint, it is believed that this is an important patent.
· Handling of BASIS (magnesium material)

6. [Evaluation by Manager]   S · A · B · C

Read and Understood by	Read and Understood by
Date:	Date:

Manager's Seal	Chief's Seal

＊ ＊ Search the prior arts by SAPIO etc. when requesting for application ＊ ＊

(a)Put this on the Labonote after filling 1 - 3 and self-signed & witnessed.
(b)Complete the form on the copy of (a) from 4 down and submit it to BU leader.
(c)Attach the copy of (b) to a request paper for application for IP division.
(d)Get the BU leader's seal and the Planning Group Chief's signature,

and forward it to IP division.

* (a)- (c) are handled by the inventor(s), and (d) are by BU leader and the Planning Group

Exhibit C

[DOCUMENT NAME] SPECIFICATION

[TITLE OF THE INVENTION] NONAQUEOUS ELECTROLYTE SECONDARY
BATTERY

[Claims]

[Claim 1]

A nonaqueous electrolyte secondary battery which has
positive and negative electrodes each containing a material
capable of storing/releasing lithium ions and a nonaqueous
electrolyte solution, said secondary battery being
characterized in that said positive active material mainly
comprises a lithium transition metal complex oxide containing
Li, Ni and Mn and having a layered structure and further
contains zirconium.

[Claim 2]

The nonaqueous electrolyte secondary battery as recited
in claim 1, characterized in that graphite material is used
as the negative electrode and that a ratio in charging capacity
(opposing portions) of said negative electrode to said positive
electrode at a charge voltage of at least 4.2V is in the range
of 1.0 - 1.3.

[Claim 3]

The nonaqueous electrolyte secondary battery as recited
in claim 1 or 2, characterized in that said positive electrode
in a fully charged state has a potential of at least 4.5 V vs.
Li/Li$^+$.

[Claim 4]

The nonaqueous electrolyte secondary battery as recited

in claim 1 or 2, characterized in that said lithium transition metal complex oxide is represented by a chemical formula: $Li_aMn_xNi_yCo_zO_2$ ($0 \leq a \leq 1.2$, $x + y + z = 1$, $0 < x \leq 0.5$, $0 < y \leq 0.5$ and $z \geq 0$).

[Claim 5]

The nonaqueous electrolyte secondary battery as recited in any one of claims 1 - 3, characterized in that said lithium transition metal complex oxide contains substantially the same amount of Ni and Mn.

[Claim 6]

The nonaqueous electrolyte secondary battery as recited in any one of claims 1 - 4, characterized in that said lithium transition metal complex oxide has a specific surface area of $0.1 - 2.0 \ m^2/g$.

[DETAILED DESCRIPTION OF THE INVENTION]

[INDUSTRIAL FIELD OF APPLICATION]

The present invention relates to a lithium secondary battery, further relates to an improvement of a positive electrode intended to improve charge-discharge cycle characteristics of a nonaqueous battery, particularly to improve charge-discharge cycle characteristics at a high potential.

[PRIOR ARTS]

In recent years, nonaqueous electrolyte secondary batteries using metallic lithium, an alloy capable of storing and releasing lithium or a carbon material as the negative active material and a lithium transition metal complex oxide represented by the chemical formula: $LiMO_2$ (M indicates a transition metal) as the positive active material have been noted as high-energy-density batteries.

A representing example of the lithium transition metal complex oxide is lithium cobaltate ($LiCoO_2$), which has been already put to practical use as the positive active material for nonaqueous electrolyte secondary batteries. However, other lithium transition metal complex oxides containing Mn or Ni as a transition metal, as well as those containing all of these three transition metal elements, have been also studied (for example, Patent Registration No. 2,561,556, Patent Registration No. 3,244,314, Journal of Power Sources, 90(2000), 176-181). Among those lithium transition metal complex oxides containing Mn, Ni and Co, the material having the same composition of Mn and Ni and represented by a chemical formula: $LiMn_xNi_xCo_{(1-2x)}O_2$ is reported as showing a uniquely high thermal stability even in a charged state (high oxidation

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state) in Electrochemical and Solid-State Letters, 4(12), A200-A203(2001). It is also reported in Patent Laying-Open No. 2002-42,813 that the complex oxide having substantially the same composition of Ni and Mn has a voltage of approximately 4 V, as comparable to that of $LiCoO_2$, and shows a high capacity and a superior charge-discharge efficiency. Batteries using a positive electrode containing, as a chief material (at least 50 % by weight), such a lithium transition metal complex oxide containing Mn, Ni and Co and having a layered structure (for example, chemical formula: $Li_aMn_bNi_bCo_{(1-2b)}O_2$ ($0 \leq a \leq 1.2$, $0 < b \leq 0.5$)), because of their high thermal stability during charge, can be expected to achieve a marked reliability improvement. Also, it is reported (Chemistry Letters, 2001, pp 642-643) that this lithium transition metal complex oxide containing Mn, Ni and Co and having a layered structure, because of its high structural stability, exhibits better cycle characteristics than currently-used $LiCoO_2$ or others, even when its charge voltage is set at a higher value (positive electrode potential of at least 4.5 V (vs. Li/Li^+)) than values used in the current state of the art. In existing nonaqueous electrolyte secondary batteries using a lithium transition metal complex oxide (for example, $LiCoO_2$) for the positive electrode, an end-of-charge voltage is generally prescribed at 4.1 - 4.2 V. In this case, the positive electrode utilizes only 50 - 60 % of its theoretical capacity. Therefore, the use of a lithium transition metal complex oxide having a layered structure enables the positive electrode to utilize at least 70 % of its theoretical capacity and thus enables the battery to increase its capacity and energy density without marked deterioration of thermal stability even when a charge voltage is set at a high value.

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[PROBLEMS TO BE SOLVED]

However, nonaqueous electrolyte secondary batteries, even if using the lithium transition metal complex oxide containing Mn, Ni and Co and having a layered structure as the positive active material, still show the declining working voltage and discharge capacity with charge-discharge cycling. Particularly in a charged state at such a high potential that a positive electrode has a charge voltage of at least 4.5 V (vs. Li/Li$^+$), such batteries exhibit marked loss in working voltage and discharge capacity after charge-discharge cycles. The resulting energy density loss has been a problem. That is, a problem in cycle characteristics has been encountered in such batteries, particularly those which have a positive electrode potential of at least 4.5 V (vs. Li/Li$^+$) in a fully charge state (e.g., those which have a charge voltage of at least 4.4 V when using a carbon negative electrode having a charge potential of 0.1 V (vs. Li/Li$^+$).

It is an object of the present invention to provide a lithium secondary battery which uses a positive electrode containing a lithium transition metal complex oxide containing Mn and Ni and having a layered structure, and which can suppress declining of working voltage and capacity during charge-discharge cycles, particularly in a charged state at such a high potential that a positive electrode has a charge voltage of at least 4.5 V (vs. Li/Li$^+$), and improve cycle characteristics.

[MEANS FOR SOLVING THE PROBLEMS]

To achieve the above object, the nonaqueous electrolyte secondary battery provided by the present invention has positive and negative electrodes each containing a material capable of storing/releasing lithium ions and a nonaqueous

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electrolyte solution, said secondary battery being characterized in that said positive active material mainly comprises a lithium transition metal complex oxide containing Li, Ni and Mn and having a layered structure and further contains zirconium.

In existing nonaqueous electrolyte secondary batteries using $LiCoO_2$ for the positive electrode, an end-of-charge voltage is generally prescribed at 4.1 - 4.2 V, and in those using carbon material for the negative electrode, a positive electrode in a fully charged state has a potential of 4.2 - 4.3 V (vs. Li/Li^+). Additionally, an opposing capacity ratio when charged at the aforementioned voltage is generally designed to fall within the range of 1.0 - 1.3 (the charge amount of the positive electrode < that of the negative electrode). The reason for this design is that if this charge capacity ratio falls below 1.0, metallic lithium may precipitate on a surface of the carbon material and alloy material to thereby deteriorate cycle characteristics and lower a safety level of the battery in a remarkable manner. On the other hand, if the charge capacity ratio exceeds 1.3, an excess part of the negative electrode that does not take part in a reaction enlarges to lower an energy density of the battery.

Therefore, in the representative example of the nonaqueous electrolyte secondary battery of the present invention, material capable of storing/releasing lithium such as carbon material and Li alloy material is used for the negative electrode, a charge voltage of the battery is at least 4.2 V, a positive electrode in a charged state has a potential of 4.3 - 5.2 V vs. Li/Li^+, the opposing capacity ratio is 1.0 - 1.3 when charged at the voltage. Meanwhile, if the positive electrode is charged to a potential range that exceeds 5.2 V vs. Li/Li^+, decomposition of the electrolyte solution on an

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electrode surface in some cases becomes more significant than extraction of lithium in the active material, therefore, a charge voltage of the positive electrode falls within the above-mentioned range.

The lithium transition metal complex oxide for incorporation of zirconium is preferably represented by a chemical formula: $Li_aMn_xNi_yCo_zO_2$ (a, x, y and z satisfy $0 \leq a \leq 1.2$, $x + y + z = 1$, $0 < x \leq 0.5$, $0 < y \leq 0.5$ and $z \geq 0$), and further preferably, nickel and manganese are contained substantially in the same amount. Also in order to restrain the positive active material at a high potential from reacting with the electrolyte solution, the positive active material preferably has a specific surface area in the range of 0.1 - 2.0 m^2/g.

A mixed solvent of a cyclic carbonate which has high-dielectric and a chain carbonate which has low viscosity is preferably used as a nonaqueous electrolyte solvent for use in the present invention. Cyclic carbonates are susceptible to oxidation decomposition at a high potential. Therefore, the cyclic carbonate content of the solvent is preferably within the range of 10 - 30 % by volume. In addition, aluminum foil which has a thickness of 10 - 30 μm is generally used as a positive current collector. When such a current collector is used, however, there is a possibility that corrosion of the foil itself progresses at a high potential of at least 4.5 V vs. Li/Li^+. Therefore, inclusion of $LiPF_6$ for supporting salt is preferred because $LiPF_6$ restrains such corrosion (this is considered to be due to fabrication of passivation film of aluminum fluoride). In addition, a higher potential of a positive electrode increases a tendency of electrolytic

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solution on a carbon surface, which is used as a conductive agent, to decompose. For this reason, an amount of carbon as a conductive agent contained in a positive electrode is desirably at most 5 wt%.

[FUNCTION]

Concerning the structure which suppresses declining of working voltage and capacity with charge-discharge cycling in a electrode using a lithium transition metal complex oxide containing Li, Mn and Ni and having a layered sutructure, though the details of this cause are not clarified, the following has been found as a result of analysis of the positive and negative electrodes after charge-discharge cycles (See reference experiments).

(1) In case of a lithium transition metal complex oxide excluding Zr and having the above-mentioned layered structure, its XRD patterns both before and after cycles show no appreciable difference.

(2) Measurement of the amount of Mn precipitated (or deposited) on a negative electrode after cycles reveals that a battery using a lithium transition metal complex oxide excluding Zr and having the above-mentioned layered structure as a positive active material contains a larger amount of Mn precipitated on negative electrode, compared to the battery of the present invention which uses a lithium transition metal complex oxide containing Zr.

It is believed from the forgoing that the declining characteristics of the battery using the lithium transition metal complex oxide containing Li, Mn and Ni and having a layered structure as a positive active material with charge-discharge cycles is not due to structural degradation

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of the positive active material but due to elution of Mn from a surface of the positive active material (precipitation of the eluted Mn on the negative electrode). This probably causes a resistance build-up at a positive electrode-electrolyte solution interface to result in loss of working voltage and discharge capacity. Although the effect of the zirconium addition on charge-discharge cycle characteristics is confirmed even in a charged state at a positive electrode potential of 4.3 V vs. Li/Li$^+$, its effect, particularly, to suppress decline of a working potential becomes more significant when in a charged state at a high potential of at least 4.5 V vs. Li/Li$^+$ (See Table 2 and Figs.2 - 5, or Tables 3 - 5).

Patent Registration No. 2,855,877 is an example of addition of Zr to lithium transition metal complex oxide represented by LiMO$_2$ (M: transition metal). However, as it describes in paragraph [0008], its action/effect is to prevent decomposition of an electrolyte solution and structural degradation of active material by coating LiCoO$_2$ particle surfaces with zirconium oxide (IV) or a lithium zirconium complex oxide so that they are stabilized, and is therefore believed to be completely different from the action/effect of the present invention.

The lithium transition metal complex oxide desirably contains substantially the same amount of Ni and Mn, in order to balance characteristics in which manganese, in its nature, is low in capacity but high in thermal stability during charge, while Nickel, in its nature, is high in capacity but low in thermal stability during charge.

If the zirconium content is excessively small, an effect

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on a charge-discharge cycle characteristics at a high potential may not be obtained sufficiently. On the other hand, if the zirconium content is excessively large, discharge characteristics of the positive electrode may be adversely affected. Therefore, the amount of zirconium contained in the positive active material is preferably from 0.1 mole % to 5 mole %, based on the lithium transition metal complex oxide.

[EMBODIMENT OF THE INVENTION]

The present invention is below described in more detail by way of Examples. It will be recognized that the following examples merely illustrate the present invention and are not intended to be limiting thereof. Suitable changes can be effected without departing from the scope of the present invention.

[EXAMPLES]

By the following methods, a three-electrode beaker cell was constructed, and charged and discharged to evaluate the charge-discharge characteristics of the electrode.

<EXPERIMENT 1>
(EXAMPLE 1)
[Preparation of Positive Active Material]

LiOH and a coprecipitated hydroxide represented by $Mn_{0.33}Ni_{0.33}Co_{0.34}(OH)_2$ were mixed in an Ishikawa automated mortar such that a ratio in mole of Li to all transition metals was brought to 1:1. Then, zirconium (IV) oxide was added so that a ratio in mole of zirconium to the obtained main active material $LiMn_{0.33}Ni_{0.33}Co_{0.34}O_2$ was brought to 0.5 %. The resulting mixture was heat treated in the air atmosphere at 1,000 ℃ for 20 hours and then pulverized to obtain a lithium

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transition metal complex oxide represented by $LiMn_{0.33}Ni_{0.33}Co_{0.34}O_2$ and having a mean particle diameter of about 10 μm. A BET specific surface area of the obtained $LiMn_{0.33}Ni_{0.33}Co_{0.34}O_2$ was 0.67 m^2/g.

[Fabrication of Working Electrode]

The above-prepared positive active material, carbon as an electrical conductor and polyvinylidene fluoride as a binder at a ratio by weight of 90:5:5, were added to N-methyl-2-pyrrolidone as a dispersing medium. The mixture was kneaded to prepare a cathode mix slurry. The prepared slurry was coated on an aluminum foil as a current collector, dried and then rolled by a pressure roll. Subsequent attachment of a current collecting tab completed fabrication of a working electrode.

[Preparation of Electrolyte Solution]

Ethylene carbonate (EC) and ethyl methyl carbonate (EMC) were mixed at a 3:7 ratio by volume to provide a solvent in which lithium hexafluorophosphate ($LiPF_6$) was subsequently dissolved in the concentration of 1 mole/liter to prepare an electrolyte solution.

[Construction of Three-Electrode Beaker Cell]

The three-electrode beaker cell shown in Figure 1 was constructed in a glove box maintained under Ar atmosphere. Metallic lithium was used for the counter electrode and reference electrode.

[Evaluation of Initial Charge-Discharge Characteristics]

The above-fabricated three-electrode beaker cell at room temperature was charged at a constant current of 0.75 mA/cm^2

(about 0.3C) until a working electrode potential reached 4.3 V vs. Li/Li$^+$, further charged at a constant current of 0.25 mA/cm^2 (about 0.1C) until the potential reached 4.3 V vs. Li/Li$^+$ and then discharged at a constant current of 0.75 mA/cm^2 (about 0.3C) until the potential reached 2.75 V vs. Li/Li$^+$ to evaluate initial charge-discharge characteristics.

[Evaluation of Charge-Discharge Cycle Characteristics]

The above evaluation of initial charge-discharge cycle characteristics was followed by 15 cycles of charge and discharge at room temperature under the same conditions and then a capacity retention on the 16th-cycle was calculated from the following equation. Also, discharge curves for the 1st-cycle and 16th-cycle were compared to determine a decline in the average electrode potential and in potential when discharge was initiated.

Capacity retention (%) = (16th-cycle discharge capacity) ÷ (1st-cycle discharge capacity) × 100

(EXAMPLE 2)

In Preparation of Positive Active Material, zirconium oxide contained in the heat-treated $LiMn_{0.33}Ni_{0.33}Co_{0.34}O_2$ was added so that a ratio in mole of zirconium was brought to 1.0 %. Otherwise, the procedure of Example 1 was followed to construct a three-electrode beaker cell. A BET specific surface area of the obtained $LiMn_{0.33}Ni_{0.33}Co_{0.34}O_2$ was 0.64 m^2/g. Its initial charge-discharge characteristics and charge-discharge cycle characteristics were evaluated in the same manner as in Example 1.

(EXAMPLE 3)

The procedure of Example 1 was followed to construct a

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three-electrode beaker cell.

The procedure of Example 1 was followed, except that the prescribed charge potential of the working electrode was 4.6 V vs. Li/Li$^+$, to evaluate initial charge-discharge characteristics and charge-discharge cycle characteristics.

(EXAMPLE 4)

The procedure of Example 2 was followed to construct a three-electrode beaker cell.

The procedure of Example 1 was followed, except that the prescribed charge potential of the working electrode was 4.6 V vs. Li/Li$^+$, to evaluate initial charge-discharge characteristics and charge-discharge cycle characteristics.

(COMPARATIVE EXAMPLE 1)

In Preparation of Positive Active Material, LiOH and the coprecipitated hydroxide represented by $Mn_{0.33}Ni_{0.33}Co_{0.34}(OH)_2$ were mixed in an Ishikawa automated mortar such that a ratio in mole of Li to all transition metals was brought to 1:1. Otherwise, the procedure of Example 1 was followed to construct a three-electrode beaker cell and evaluate initial charge-discharge characteristics and charge-discharge cycle characteristics.

(COMPARATIVE EXAMPLE 2)

The procedure of Comparative Example 1 was followed to construct a three-electrode beaker cell.

The procedure of Example 1 was followed, except that the prescribed charge potential of the working electrode was 4.6 V vs. Li/Li$^+$, to evaluate initial charge-discharge characteristics and charge-discharge cycle characteristics.

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The evaluation results for initial charge-discharge characteristics and charge-discharge cycle characteristics of beaker cells A1 – A4 in the above Examples 1 – 4 and beaker cells X1 and X2 in the Comparative Examples 1 and 2 are shown in Tables 1 and 2 and Figures 2 - 5. In Table 1, the specific surface area of the positive active material prepared by the examples and comparative examples is also shown.

(Table 1) Initial charge-discharge characteristics for batteries of Examples 1 – 4 and Comparative Examples 1 - 2

	Cell	Zr Content (Mole %) of Active Material	End-of-Charge Voltage (V vs.Li/Li$^+$)	Specific Surface Area (m^2/g)	Initial Charge /Discharge Efficiency (%)	Discharge Capacity (mAh/g)	Average Electrode Potential (V vs. Li/Li$^+$)
Comp. Ex. 1	X1	0	4.3	0.67	84.5	149.0	3.784
Ex. 1	A1	0.5		0.67	85.0	149.4	3.809
Ex. 2	A2	1.0		0.63	85.6	150.8	3.806
Comp. Ex. 2	X2	0	4.6	0.67	84.5	186.8	3.928
Ex. 3	A3	0.5		0.67	85.1	186.7	3.927
Ex. 4	A4	1.0		0.63	84.9	187.4	3.923

(Table 2) Evaluation results of charge-discharge characteristics for batteries of Examples 1 – 4 and Comparative Examples 1 - 2

	Cell	Zr Content (Mole %) of Active Material	End-of-Charge Voltage (V vs.Li/Li$^+$)	Loss of Discharge Initiating Potential before and after Cycles (mV)	Loss of Average Electrode Potential before and after Cycles (mV)	Capacity Retention (%)
Comp. Ex. 1	X1	0	4.3	56	14	94.5
Ex. 1	A1	0.5		15	16	97.7
Ex. 2	A2	1.0		14	21	97.1
Comp. Ex. 2	X2	0	4.6	156	94	89.2
Ex. 3	A3	0.5		55	46	93.1
Ex. 4	A4	1.0		64	51	92.5

As evident from Table 2, addition of zirconium improves capacity retention of $LiMn_{0.33}Ni_{0.33}Co_{0.34}O_2$ in charge-discharge cycles and restrains a decline of a discharge initiating potential. As can be appreciated from comparison between

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Examples 1 - 2 and Examples 3 - 4, Examples 3 -4 in which the end-of-charge potential is at least 4.5 V vs. Li/Li$^+$ is much more effective to improve a decline of a discharge initiating potential by about 100 mV, compared to the zirconium-excluded Comparative Example 2.

As evident from Table 2 and Figs. 2 - 5, concerning the degree of declining an average electrode potentials before and after charge-discharge cycles, the effect of the zirconium addition is not confirmed at the end of charge of 4.3 V vs. Li/Li$^+$. On the other hand, with increase in content of zirconium, it has been found that decline of an average electrode potential is suppressed at the end of charge of 4.6 V vs. Li/Li$^+$.

In this way, it turned out that the zirconium addition is particularly effective at a higher charge voltage (when the positive electrode has a potential of 4.2 - 4.3 V vs. Li/Li+) than at the conventional charge voltage (when the positive electrode has a potential of at least 4.5V vs. Li/Li+).

<EXPERIMENT 2>

By the following methods, a battery was constructed to evaluate its initial charge-discharge characteristics and charge-discharge cycle characteristics.

(EXAMPLE 5)
[Fabrication of Positive Electrode]

The positive active material prepared in Example 2, carbon as an electrical conductor and polyvinylidene fluoride as a binder at a ratio by weight of 90:5:5 were added to N-methyl-2-pyrrolidone as a dispersing medium. The mixture was kneaded to prepare a cathode mix slurry. The prepared

slurry was coated on an aluminum foil as a current collector, dried and then rolled by a pressure roll. Subsequent attachment of a current collecting tab completed fabrication of a positive electrode.

[Fabrication of Negative Electrode]

Synthetic graphite as the negative active material and a styrene-butadiene rubber as a binder were added to an aqueous solution of carboxymethylcellulose as a thickener so that the mixture contained the active material, binder and thickener in the ratio by weight of 95:3:2. The mixture was then kneaded to prepare an anode mix slurry. The prepared slurry was coated onto a copper foil as a current collector, dried and rolled by a pressure roll. Subsequent attachment of a current collecting tab completed fabrication of a negative electrode.

[Preparation of Electrolyte Solution]

Ethylene carbonate (EC) and ethyl methyl carbonate (EMC) were mixed at a 3:7 ratio by volume to provide a solvent in which lithium hexafluorophosphate ($LiPF_6$) was subsequently dissolved in the concentration of 1 mol/1 to prepare an electrolyte solution.

[Construction of Battery]

The above-obtained positive and negative electrodes were wound, while interposing a separator between them, to provide a wound assembly. In a glove box maintained under Ar atmosphere, the wound assembly and electrolyte solution were encapsulated in a casing of an aluminum laminate to obtain a nonaqueous electrolyte secondary battery A5 having a battery standard size of 3.6 mm in thickness, 3.5 cm in width and 6.2 cm in length. The ratio in charge capacity of the negative

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to positive electrode in their portions opposed to each other was 1.15.

(COMPARATIVE EXAMPLE 3)

The procedure of Example 5 was followed, except that the positive active material in Comparative Example 1 was used, to construct a battery and evaluate its characteristics.

[Evaluation of Initial Charge-Discharge Characteristics of Battery]

The constructed nonaqueous electrolyte secondary battery at room temperature was charged at a constant current of 650 mA (about 1.1C) to a voltage value of 4.5 V, further charged at a constant voltage of 4.5 V to a current value of 32 mA (about 0.06C) and then discharged at a constant current of 650 mA to a voltage value of 2.75 V to thereby measure its discharge capacity (mAh).

[Evaluation of Charge-Discharge Cycle Characteristics]

After evaluation of the initial charge-discharge cycle characteristics, the battery was subjected to a charge-discharge cycle test under the same conditions to determine its capacity retention and change in discharge initiating voltage on the 50th-cycle. The results are shown in Table 3. The capacity retention was calculated from the following equation.

Capacity retention (%) = (50th-cycle discharge capacity) ÷ (1st-cycle discharge capacity) × 100

(Table 3) Evaluation results of battery characteristics

	Cell	Charge Voltage (V)	Zr Content (Mole %) of Active	Initial Discharge Capacity (mAh)	Initial Charge /Discharge Efficiency (%)	Capacity Retention (%) after	Loss of Discharge Initiating Potential before and after Cycles

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			Material			50 Cycles	(mV)
Ex. 5	A5	4.5	1.0	642.7	82.1	92.2	67
Comp. Ex. 3	X3	4.5	0	629.7	83.0	91.3	95

As evident from Table 3, the Zr-incorporated battery of Example 5 of the present invention shows the improved capacity retention after 50 cycles and the reduced a decline of discharge initiating voltage after cycles, compared to the Zr-excluded battery of Comparative Example 3.

<REFERENCE EXPERIMENTS>

The following experiment was conducted to investigate the cause of the decline of working voltage and discharge capacity when a lithium transition metal complex oxide containing Li, Mn and Ni and having a layered structure is subjected to charge-discharge cycles and also investigate the action/effect of incorporating zirconium.

① Measurement of XRD of positive active material before and after charge-discharge cycles

The positive electrode was removed from the battery X3 of Comparative Example 3 before and after charge-discharge cycles and its X-ray diffraction was carried out using CuKα radiation as the source. The results are shown in Figure 6. The half width was also calculated using a lattice constant and a Gauss method. The results are shown in Table 6.

(Table 4)Lattice constant and Half-Width of positive electrode before and after charge-discharge cycles

	Battery	Charge-Discharge Cycles	Half-Width (deg)		
			(003)Plane	(104)Plane	(110)Plane
Comp. Ex.3	X3	before Cycles	0.1423	0.2244	0.2555
	X3	after Cycles	0.1539	0.2444	0.3006

As can be clearly seen from Figure 6, a difference between X-ray diffraction patterns of the positive active material of the battery before and after charge-discharge cycles is not appreciable. As can also be clearly seen from Table 4, there is no appreciable difference in half width of the positive active material of the battery before and after charge-discharge cycles. These are believed to suggest that no degradation has occurred in a crystal structure of the positive active material of the battery after cycles.

② Measurement of amount of Mn precipitated on negative electrode of battery after cycles

After charge-discharge cycles, each of the battery of Example 5 and the battery of Comparative Example 3 was disassembled to collect its negative electrode. Then, the amount of Mn precipitated on a surface of the negative electrode was measured by fluorescent X-ray analysis using rhodium radiation as the source (a range of detection is 0 - 40 keV). The results are shown in Table 4.

(Table 5) Evaluation results of battery characteristics

	Zr Content (Mole %) of Active Material	Amount of Mn Precipitated on Negative Electrode (cps/μA)
Ex. 5	1.0	1.901
Comp. Ex. 3	0	2.262

As evident from Table 4, the amount of manganese precipitated on the negative electrode of the zirconium-incorporated battery of Example 5 is more than 10 % smaller than that of the zirconium-excluded battery of Comparative Example 3. It is believed from the forgoing results

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of these reference experiments that the declining working voltage and discharge capacity of the battery having a lithium transition metal complex oxide containing Li, Mn and Ni and having a layered structure with charge-discharge cycling is not due to the degradation of crystal bulk structure of the positive active material when subjected to charge-discharge cycles but due to the elution of Mn from the positive active material when subjected to charge-discharge cycles (and the resulting resistance build-up at the interface between the positive electrode and the electrolyte solution). Like the positive active material of the examples, containing zirconium is inferred to retard elution of Mn and restrain declining of working voltage and discharge capacity with charge-discharge cycling as mentioned above.

[EFFECT OF THE INVENTION]

As described in detail above, it is possible to provide a nonaqueous electrolyte secondary battery which has a positive electrode and a negative electrode containing material capable of storing/releasing lithium ions and a nonaqueous electrolyte solution, in which the positive active material mainly comprises a lithium transition metal complex oxide containing Li, Ni and Mn and having a layered structure, and which suppresses declining of discharge voltage and capacity during charge-discharge cycles and improves cycle characteristics by inclusion of zirconium in the lithium transition metal complex oxide in the positive active material.

[BREIF DESCRIPTION OF THE DRAWINGS]
[Fig. 1] A schematic view showing a three-electrode beaker cell.
1: working electrode, 2: counter electrode (lithium metal),

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3: reference electrode (lithium), 4: electrolyte solution

[Fig. 2] A graph showing 2nd-cycle and 16th-cycle charge/discharge curves for the batteries of Example 1 and Comparative Example 1 (A1, X1): an end of charge of 4.3 V vs. Li/Li$^+$.

[Fig. 3] A graph showing 2nd-cycle and 16th-cycle charge/discharge curves for the batteries of Example 2 and Comparative Example 1 (A2, X1): an end of charge of 4.3 V vs. Li/Li$^+$.

[Fig. 4] A graph showing 2nd-cycle and 16th-cycle charge/discharge curves for the batteries of Example 3 and Comparative Example 2 (A3, X): an end of charge of 4.6 V vs. Li/Li$^+$.

[Fig. 5] A graph showing 2nd-cycle and 16th-cycle charge/discharge curves for the batteries of Example 4 and Comparative Example 2 (A4, X2): an end of charge of 4.6 V vs. Li/Li$^+$.

[Fig. 6] A chart showing X-ray diffraction pattern of the positive electrode of the battery (X3) of Comparative Example 3 before and after the charge-discharge cycle test.
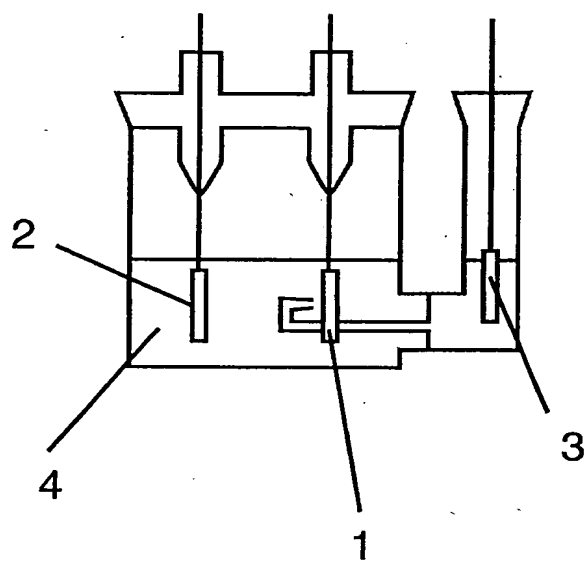
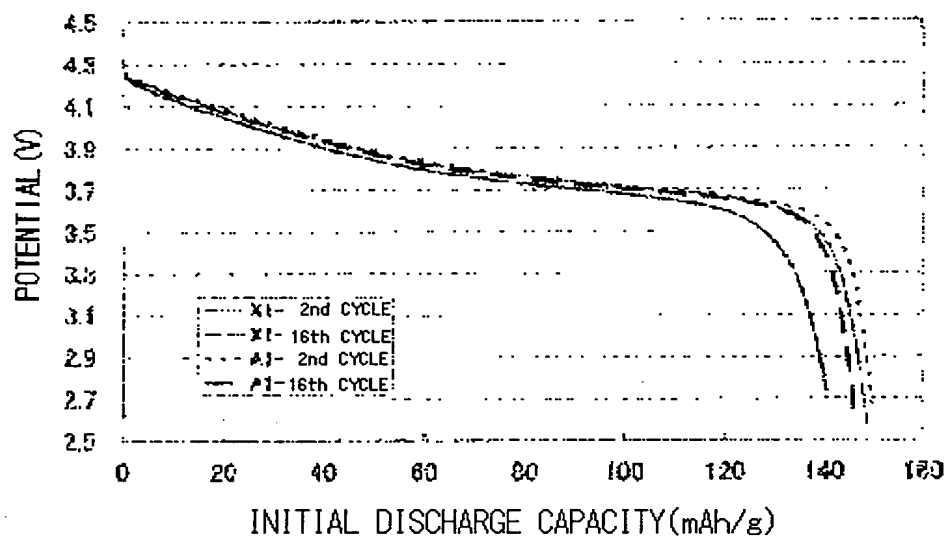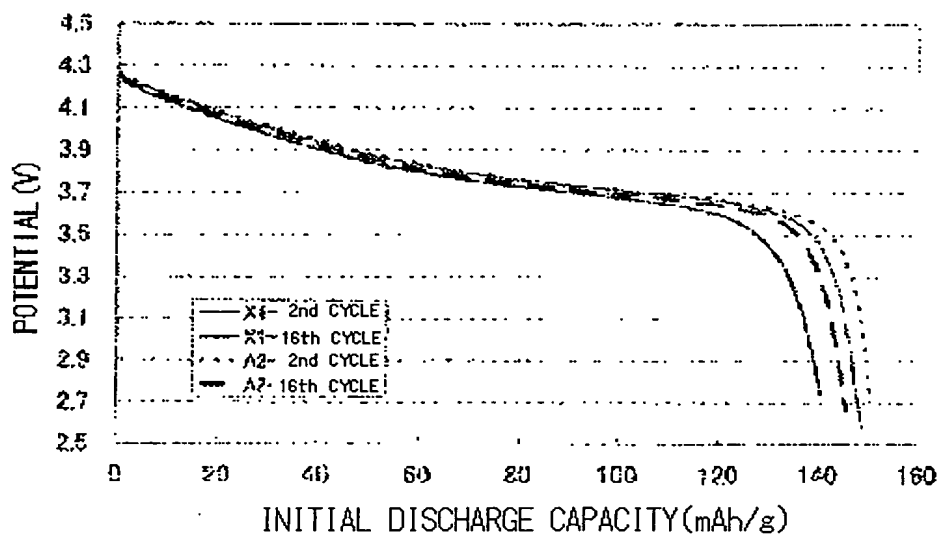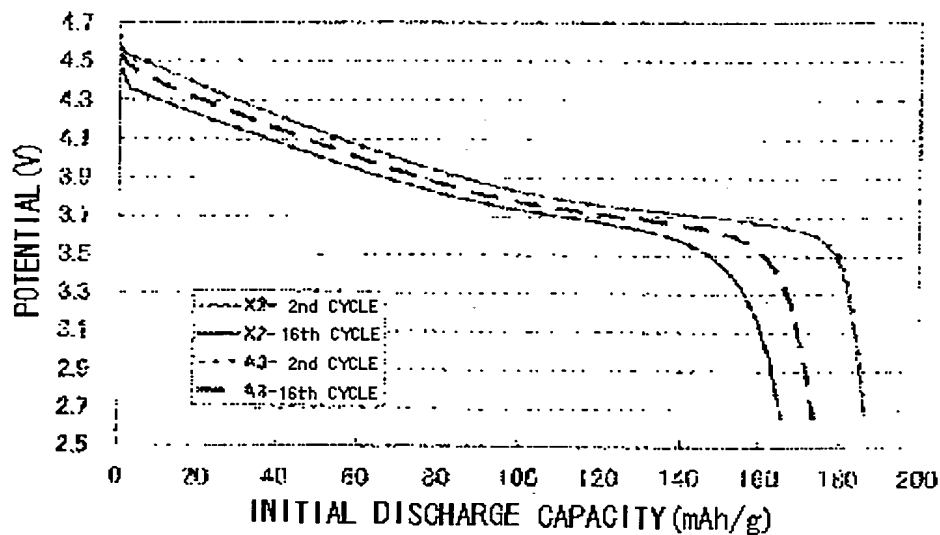Fig. 1   A schematic view of a three-electrode beaker cell

Fig.2 A graph showing 2nd-cycle and 16th-cycle charge/discharge curves for
the batteries of Example 1 and Comparative Example 1 (A1, X1): an end of charge of 4.3 V vs. Li/Li+

Fig.3 A graph showing 2nd-cycle and 16th-cycle charge/discharge curves for
the batteries of Example 2 and Comparative Example 1 (A2, X1): an end of charge of 4.3 V vs. Li/Li+

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Fig.4 A graph showing 2nd-cycle and 16th-cycle charge/discharge curves for the batteries of Example 3 and Comparative Example 2 (A3, X2): an end of charge of 4.8 V vs. Li/Li+
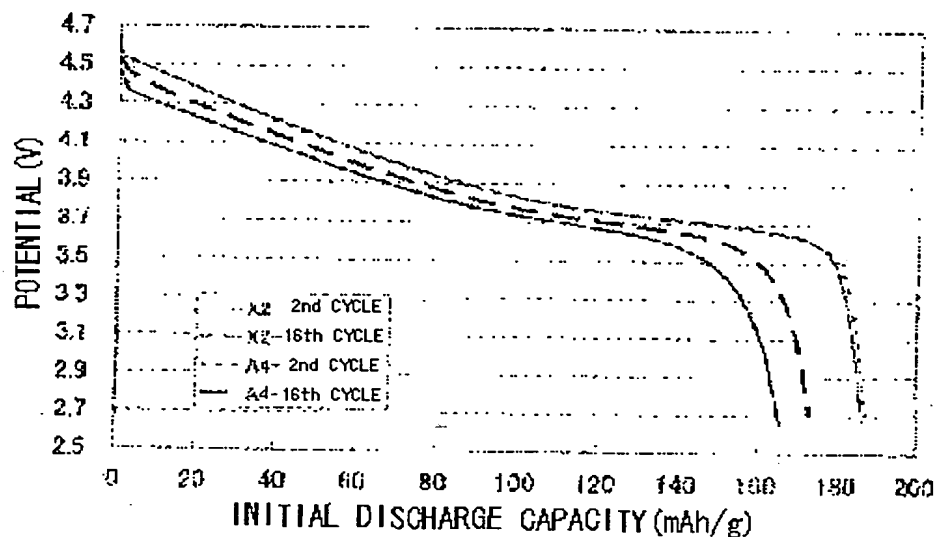

Fig.5 A graph showing 2nd-cycle and 16th-cycle charge/discharge curves for the batteries of Example 4 and Comparative Example 2 (A4, X2): an end of charge of 4.8 V vs. Li/Li+
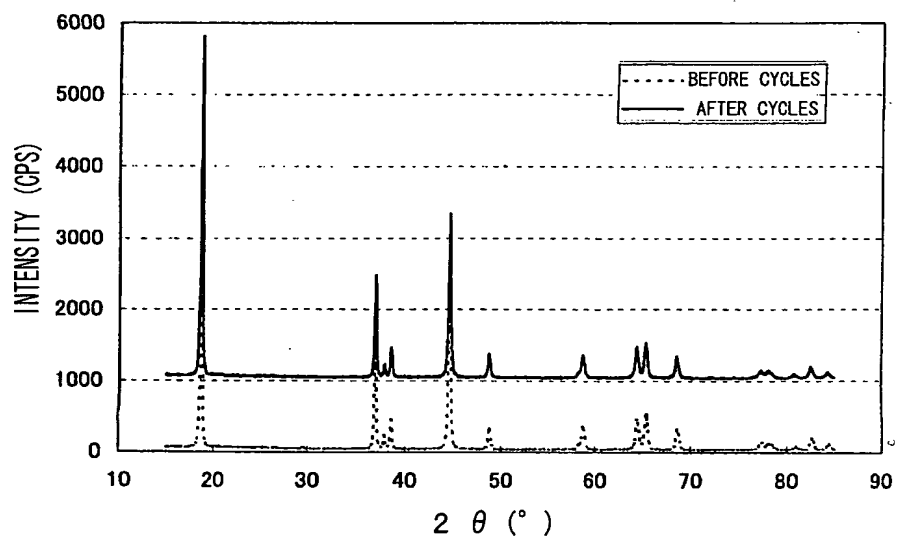
Fig.6 A chart showing X-ray diffraction patter of the positive electrode of the battery (X3)
of Comparative Example 3 before and after the charge-discharge cycle test